A review analyzing the industrial biodiesel production practice starting from vegetable oil refining

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A review analyzing the industrial biodiesel production practice starting from vegetable oil refining

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Abstract

One of the most promising renewable fuels proposed as an alternative to fossil diesel is biodiesel. The competitive potential of biodiesel is limited by the price of vegetable oils, which strongly influences the final price of this biofuel. On the other hand, extensive use of vegetable oils may cause other significant problems such as starvation in developing countries. Appropriately planning and designing the whole production process, from the seed to the biodiesel end-product, is essential to contain the influence of energy inefficiencies on the high price of the end-product. The present study reviews the technologies currently used in the production of biodiesel. We first discuss the technologies for extracting the vegetable oil from the seed, and its subsequent refining and conversion into biodiesel. This study focuses on the characteristics of the production processes currently used in the sector, illustrating the technological options and emphasizing the drawbacks of certain practices and the best choices available. The vegetable oils tend to be processed using procedures that are well established, but oriented more towards obtaining products suitable for the foodstuffs industry, and that consequently use technologies that are sometimes excessive for energetic purposes. The processes for extracting the vegetable oil from the seed generally include a set of steps, the complexity of which depends on the raw material. Basically, the two extraction technologies involved rely on the use of pressure or solvents. In practice, the two systems are often combined. Using the vegetable oils as a source of energy makes some of these steps superfluous and enables technologies to be used that would be unsuitable for foodstuffs production. This study focuses on feasible technological improvements that would give rise to oil that is still suitable for use as a source of energy, but at a lower cost. The refined vegetable oil can subsequently be converted into biodiesel by means of a great variety of technologies, many of which are still not suitable for applications on an industrial scale. The solution that has met with the greatest favor is homogeneous alkaline transesterification with KOH and methanol. Even when dealing with this type of conversion alone, it is impossible to establish a universal schema to describe the conversion or purification stages because there are numerous possible different solutions. When we then look more closely at the state of the art in industrial biodiesel production plants, we encounter the potential problems introduced by the type and characteristics of the original raw material. Comparing some of the reference solutions that have inspired numerous installations, a sensitivity analysis is conducted on the main elements involved in the process, focusing on their behavior in different working conditions to obtain products with the characteristics required by the international standards (EN 14214:2008, ASTM D 6751 07b).

Keywords: biodiesel, production process, industrial practice, vegetable oil refining, biodiesel refining, transesterification

Contents

1. Introduction

Crude oil is a non-renewable resource that will eventually run out. In the meantime, the steady increase in its consumption, the depletion of the reserves and the uncertain political situation in some oil-producing countries are leading to a rapid increase in the cost of crude oil.

Alternatives to oil are renewable energy sources and, among these, vegetable oils and their energy derivatives [1, 2] and biodiesel, in particular are regarded as the most promising. Biodiesel has the advantage of not being responsible for any emission of CO_2 connected with its use. As a matter of

fact, the CO_2 released into the atmosphere by biofuel combustion is the same CO_2 that was absorbed by photosynthesis by the growing plant. In addition, the CO emissions are more limited than from fossil diesel, while a slightly higher level of NO_x emissions can be expected [3].

However renewable fuels cannot replace fossil fuels for the time being, they can only contribute to reduce the latter's consumption [4]. Even if all the animal and vegetable fats currently available on the market were to be converted into biofuel, this would still only cover a limited part of the demand for fuel [5]. Moreover, the chances of the price of biodiesel being able to compete with fossil diesel are limited by the price of vegetable oil, which accounts for about 80% [6-8] of the final price of the biofuel. Although day-to-day variations in the commodities market can naturally change these considerations, Fig. 1 shows that the price of crude oil is still lower than that of refined vegetable oil [9-11] primarily due to the link between crude petroleum oil, vegetable oil refining process and speculation [12]. Actually the cost-effectiveness of using biodiesel relies entirely on its exemption from taxation [13]. An even more pressing problem, however, concerns the debate on the morality of using fertile land to grow biomass for conversion into energy instead of food crops, while so many people around the world go hungry [14].

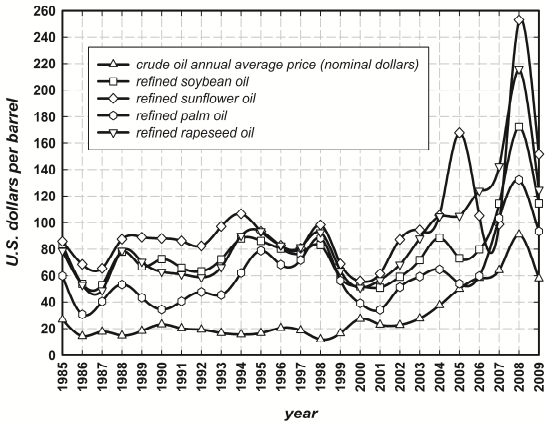

Fig. 1: Prices of some refined vegetable oil varieties.

Most of the vegetable oil currently used as biodiesel feedstock could also be used as edible oil, and this introduces a new variable in the food commodities market (which is already under strain), preventing any proper control over the prices of basic commodities intended for human nutrition. The most likely way to escape this dangerous contradiction is to completely separate the agro-energy business from the agro-food business [15, 16]. This can feasibly be done by intensive microalgae farming schemes: although this is still in the experimental phase as a biodiesel feedstock source, it has revealed far better features than land crops in terms of yield per cultivated area [17, 18].

Microalgae are an excellent alternative to land crops for a number of reasons: i) they grow year-round; ii) their yield in terms of oil per unit of cultivated area is significantly higher; iii) they can be grown on land unsuitable for food crops;

While we wait for the microalgae to reveal their full potential due to several technical problems [19, 20], we must get by with the biodiesel produced entirely from land crops. A proper production process planning and design (from seed to vegetable oil, to biodiesel) are consequently the fundamental to reduce the energy inefficiencies that strongly influence the final price of this product.

To seek ways to reduce these production costs, this paper analyses the whole chain leading from seed to biodiesel from a technical standpoint, starting with the following technological issues:

- considering the plant process flow diagram currently used in industrial applications, a proper set-up of the process parameters can ensure effective energy savings with no negative fallout on product quality;
- current industrial practice often relies on procedures designed to obtain food-grade quality, which is too high for energy purposes;
- even if the production process can be said to be sufficiently standardized, different biodiesel producers use their own parameters and solutions to optimize the yield, costs and quality of their end-product.

The present paper describes the main techniques and technologies on the industrial landscape and characterizes the main procedures in the process for obtaining biodiesel from vegetable oil, with a view to establishing the optimal process parameters and showing how the quality change with different operating conditions.

2. Characteristics of vegetable oils

On Earth there are over 4000 vegetable species from which vegetable oil can be extracted. Some of the most common crops are listed in table 1 [21] in ascending order of their yield per hectare.

Table 1:
Annual oil yield per cultivated hectare [kg ha^{-1}]

Crop		Crop		Crop	
Maize	145	Pumpkin	449	Opium	978
Lupine	195	Mustard	481	Rape	1000
Hibiscus	230	Camelina	490	Olive	1019
Calendula	256	Sesame	585	Ricin	1188
Cotton	273	Safflower	655	Jojoba	1528
Hemp	305	Rice	696	Jatropha	1590
Soy	375	Walnut	790	Avocado	2217
Coffee	386	Sunflower	800	Coconut	2260
Flax	402	Cocoa	863	Palm	5000
Hazelnut	405	Peanuts	890		

Oil from these crops contains 90-98% acylglycerols [22], a class of saponifiable and neutral lipids. The acylglycerols are characterized by the acyl group and are divided into monoacylglycerols, diacylglycerols and triacylglycerols, according to the three functions of alcoholic glycerol, which are esterified respectively with one, two or three fatty acids. The acyl chain represents 85-88% of the total weight of a triacylglycerol, depending on the type of fat, and they can be divided into saturated and unsaturated fatty acids [23]. Table 2 shows the most common fatty acids found in fats, oils and biological membranes.

Table 2:
Most common fatty acids in vegetable oil and biological membranes

Trivial name	Systematic name	CN:DB*	Structure
Unsaturated fatty acids			
Capronic acid	Hexanoic acid	6:0	$CH_3(CH_2)_6COOH$
Caprylic acid	Octanoic acid	8:0	$CH_3(CH_2)_8COOH$
Lauric acid	Dodecanoic acid	12:0	$CH_3(CH_2)_{10}COOH$
Myristic acid	Tetradecanoic acid	14:0	$CH_3(CH_2)_{12}COOH$
Palmitic acid	Hexadecanoic acid	16:0	$CH_3(CH_2)_{14}COOH$
Stearic acid	Octadecanoic acid	18:0	$CH_3(CH_2)_{16}COOH$
Arachidic acid	Eicosanoic acid	20:0	$CH_3(CH_2)_{18}COOH$
Saturated fatty acids			
Caproleic acid	9-Decenoic acid	10:1	$CH_2=CH(CH_2)_7COOH$
Palmitoleic acid	9-Hexadecenoic acid	16:1	$CH_3(CH_2)_5CH=CH(CH_2)_7COOH$
Oleic acid	cis-9-Octadecenoic	18:1	$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$
Linoleic \acid	9,12-Octadecadienoic acid	18:2	$CH_3(CH_2)_4(CH=CHCH_2)_2(CH_2)_6COOH$
Linolenic acid	6,9,12-Octadecatrienoic acid	18:3	$CH_3CH_2(CH=CHCH_2)_3(CH_2)_6COOH$
Arachidonic acid	5,8,11,14-Eicosatetraenoic acid	20:4	$CH_3(CH_2)_4(CH=CHCH_2)_4(CH_2)_2COOH$

*****CN is the number of carbon atoms in molecule, DB is the number of double bond between carbon atoms.

The thermophysical properties of triacylglycerols at temperatures between 20°C and 70°C, and at ambient pressure, are of interest in the study of the biodiesel production process but not readily available because interest has always focused on the properties of triacylglycerols at high temperatures and pressures [24], mainly deriving from studies on hydrogenation [25]. So little reliable information is available on the feedstock side of the biodiesel process, i.e. the triacylglycerols [26].

The thermodynamic data needed for a sufficient characterization of the acylglycerols are requested by the process simulation tools. In fact, often these simulation tools use correlation derived by a limited number of experimental data, giving results affected by not negligible errors. The experimental data present in literature are still few and especially on the compounds with oleic acid (tri-olein, di-olein, mono-olein) taken as “model compounds”. Conversely, there is an abundance of data available on the output side of the biodiesel production process. In table 3 are listed some thermodynamic experimental data measured on tri-olein, di-olein, mono-olein. Many values are still lacking.

Table 3:
Some experimental thermodynamic data of tri-olein, di-olein and mono-olein

		Tri-olein	Ref	Note	dev	Di-olein	Ref	Note	dev	Mono-olein	Ref	Note
kg/kmol	Molecular Weight	885.43	[27]			620.99	[27]			356.54	[27]	
K	Critical Temperature	--	--	--	--	--	--	--	--	--	--	--
Pa	Critical Pressure	--	--	--	--	--	--	--	--	--	--	--
m³/kmol	Critical Volume	--	--	--	--	--	--	--	--	--	--	--
	Critical Compressibility Factor	--	--	--	--	--	--	--	--	--	--	--
K	Melting Point	278.15[A]	[28]		<3%	294.65[B]	[29]		<1%	305.15[C]	[30]	
K	Triple Point Temperature	--	--	--	--	--	--	--	--	--	--	--
Pa	Triple Point Pressure	--	--	--	--	--	--	--	--	--	--	--
K	Normal Boiling Point	--	--	--	--	--	--	--	--	--	--	--
m³/kmol	Liquid Molar Volume (298.15K)	0.974	[31]	--	<5%	0.677	[31]	--	<5%	0.378	[31]	at triple point
J/kmol	Std Heat of Formation	--	--	--	--	--	--	--	--	--	--	--
J/kmol	Std Gibbs Energy of Formation	--	--	--	--	--	--	--	--	--	--	--
J/kmol·K	Std Absolute Entropy	--	--	--	--	--	--	--	--	--	--	--
J/kmol	Heat of Fusion at MP	9.41E+07	[32]		<3%							
J/kmol	Heat of Combustion	--	--	--	--	--	--	--	--	--	--	--
	Acentric Factor	--	--	--	--	--	--	--	--	--	--	--
C·m	Dipole Moment	1.05E-29	[33]	in benzene at 303 K.	N.D.							
m²/kmol	Van der Waals Area	--	--	--	--	--	--	--	--	--	--	--
m³/kmol	Van der Waals Volume	--	--	--	--	--	--	--	--	--	--	--
	Refractive Index	1.467	[34]	--	<0.2%	1.4663	[35]	at 295 K	<0.2%	1.463	[36]	at 293 K
K	Flash Point	--	--	--	--	--	--	--	--	427	[37]	
	Dielectric Constant	3.109	[38]	at 293.15 K.	N.D.	--	--	--	--	--	--	--
J/kmol·K	Heat Capacity, Solid (298.15K)	--	--	--	--	--	--	--	--	--	--	--
N/m	Surface Tension (298.15K)	0.0343	[31]	Error<5%	0.3(min)-0.7(max)		--	--	--	--	--	--
W/m·K	Thermal Conductivity, Liquid (298.15K)	0.1713	[31]	Error<5%	0		--	--	--	--	--	--
Pa	Vapor Pressure, Liquid (298.15K)	34.3673	[31]	Error<50%	0.2(min)-0.3(max)		--	--	--	--	--	--
Pa·s	Viscosity, Liquid (298.15K)	0.06896	[31]	Error<10%	0	--	--	--	--	--	--	--

N.D.:Not Declared

A: For the beta or triclinic form. For the beta prime or orthorhombic form use 261.15 K. For the alpha or hexagonal form use 239.15 K.

B: For the beta form

C: For the stable form I. Form II melts at 298.15 K . Form III (vitreous form) melts at 285.65 K.

On average, biodiesel produced from vegetable oils consists of a mixture of esters of fatty acids with a number of carbon atoms from 14 to 22 and various levels of unsaturation. The unsaturation gives the biodiesel variable thermophysical properties, which have been increasingly investigated in experimental studies[39-42].

3. Industrial scale production of vegetable oils

Vegetable oils are produced on an industrial scale using processes that depend on both the physical and the chemical characteristics of the feedstock. All seeds contain fat, but few of them contain fat in quantities large enough to make its extraction convenient.

The purpose of extraction techniques is to separate the fats from the proteins (which are mutually immiscible) with the greatest degree of purity at the lowest cost, avoiding any side reactions. The vegetable oils emerging from the refining process mainly comprise acylglycerols, free fatty acids, phospholipids, steroids, water and other compounds [43]. Storing the seeds is the first step in the extraction process, since any raw material decay phenomena (mould formation, lipolytic enzyme activation, etc.) need to be carefully avoided. To do so, the seeds' water content is maintained at 5-7% wt by means of drying in hot-air furnaces [44]. Then the seeds are cleaned to remove any coarse impurities in order to achieve a good product quality and protect the equipment in the plant. Before oil extraction starts, most of the seeds are treated to remove their ligno-cellulosic outer protective layer. To make the oil spill smoother, it is important to maintain the low humidity level achieved during the initial drying phase. The extraction technologies are generally characterized by a series of operations whose complexity depends on the morphology of the raw material, but there are substantially two extraction techniques [45]:

- mechanical, i.e. driven by pressure: it preserves the special characteristics of the foodstuff and residual product. The seeds are fed into an extruder that compresses the seeds, warming them in the process. A preliminary crushing action is often used before reaching the extruder in the case of oilseeds with high oil content. Discontinuous or continuous presses are used. In the first case, now applied just to olive seeds [46] or to other seeds but just in developing countries [47], the pressure applied is around 30-40 bar and the temperatures close to 95°C. In the second case, pressures as high as 400 bar can be reached in combination with temperatures up to 120-155°C [48, 49]. The press type depends on the raw material. Seeds with a high oil content are usually fully or partially treated by mechanical means. Full extraction leaves a minimum oil content in the press cake of 5-12% wt, while partial mechanical extraction leaves an oil content of about 20% wt in the cake [50].The by-product from extraction is usually cooled and used as animal feed.

- chemical, i.e. involving a solvent. The oil within the cells is difficult to extract, demanding a very slow diffusion process. Careful pre-treatment (lamination, crushing, conditioning, etc) of the raw material is of paramount importance for the diffusion process, which is also influenced by the type of solvent used [51]. Commonly used solvents include n-hexane [52], white spirit, trichloroethylene, carbon sulfide and biosolvents [53, 54]. Plants usually operate continuously and the systems can be classified as immersion, percolation or mixed immersion-percolation (Fig. 2). In immersion plants, the raw material is immersed directly in a counter-current flow of solvent. In this system is the materials can be used without any pretreatment. In percolation plants, the flow of solvent moves rapidly over the surface of the raw material. This procedure can produce oil-rich mixtures (up to 35% wt). Mixed immersion-percolation plants were developed to treat seeds with high oil content. They consist of two parts, the first removes the majority of the vegetable oil by percolation, and then the second extracts the remaining oil by immersion. There are also discontinuous plants consisting of sets of extractors with various capacities where the oil is extracted by immersion. The mixture being treated passes from one extractor to the next, gradually becoming richer in oil.

The mechanical method produces better-quality oil while the chemical one ensures greater yields.

In practice, the two systems are often combined. Mechanical extraction is generally used for seeds containing lipids in quantities exceeding 20% wt and residual in the waste product around 10-15%. Chemical extraction is used if the lipids content is below 20% wt and residual lower than 2%.

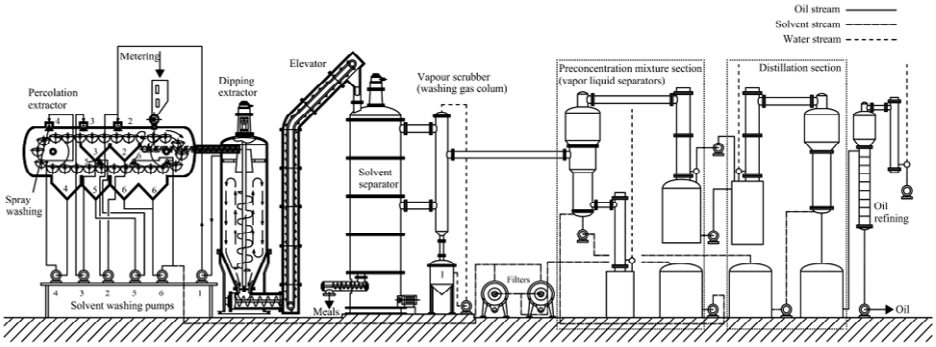

Fig. 2: Mixed immersion-percolation plant process flow diagram with solvent extraction method.

3.1 Common vegetable oil refining processes

After extraction, the oil-rich mixture goes through units to remove unwanted compounds (proteins, gums, resins, phosphates, ketones, aldehydes). The impurities are generally large particles in suspension (pieces of plant tissue, mucilages, resinous products), fine colloidal particles (invisible in

transparent oil), free fatty acids produced by acylglycerols hydrolysis and colored and semi-volatile substances dissolved in the oil. The unwanted compounds are removed by means of the treatments of purification, mucilage removal, de-acidification, bleaching, deodorization. Purification involves removing any water and impurities in suspension. This can be achieved by low-temperature sedimentation or filtering with press filters or centrifugation.

The purpose of removing mucilage (degumming) is to eliminate the phosphates and other compounds without reducing the oil acidity. Mucilage can be removed by treatment with: (a) H_2SO_4 at various concentrations; (b) water (hydration) or aqueous solutions of electrolytes; (c) adsorbent materials. In the case of hydration, the oil is mixed with very hot water, which hydrates the phospholipids, yielding an insoluble solid sediment that precipitates and can be separated with a centrifugation. The degummed vegetable oil must then be dried to remove the residual water.

Deacidification (neutralization) is used to obtain a pH-neutral oil. Various technologies are used for this purpose, i.e.

- neutralization with alkali;
- deacidification with selective solvents;
- neutralizing distillation;
- esterification of free fatty acids with glycerine.

Neutralization with alkali is the most often-used method for neutralizing oils. The process is typically discontinuous and the vegetable oil is mixed with an aqueous NaOH solution in excess of 10% wt at 60-80°C. The mass is slowly shaken to promote the reaction that converts the free fatty acids into soaps, while preventing any formation of oil-soap emulsions. In the discontinuous process the alkaline treatment takes place in reactors with a conical base to promote the separation of the neutral soap phase. The continuous process is faster and less oil is lost, but it is more complex and the plant-related costs are higher. There are several continuous neutralization methods (Sharples, Short Mix, Long Mix), but the main common steps are:

- hydration of the mucilage, with or without separation;
- a preliminary coarse neutralization and soap separation;
- a refined neutralization and soap separation;
- rinsing with water and separation of the water;
- vacuum drying.

Any oils are bleached to remove most of their pigments. Final deodorization and winterization remove any odoriferous substances (Fig. 3) and acylglycerols with high melting point [55].

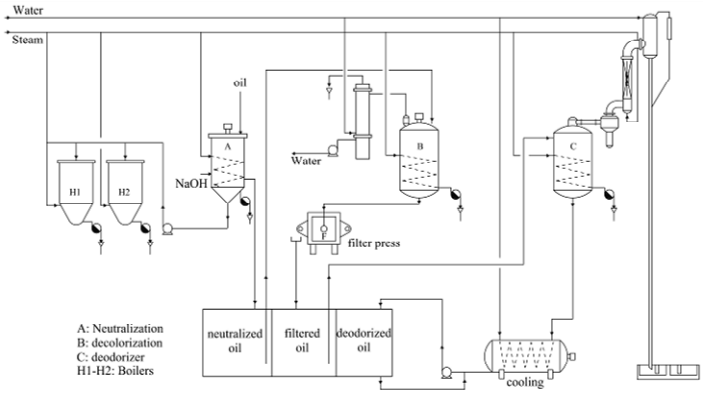

Fig. 3: Process flow diagram of a conventional vegetable oil refining plant.

3.2 Processing cost and market of refined vegetable oil

In Fig. 4 the rapeseed oil is taken as reference to compare the price of the seeds with the price of the vegetable oil (degummed) and meal to understand the value added by the refining process.

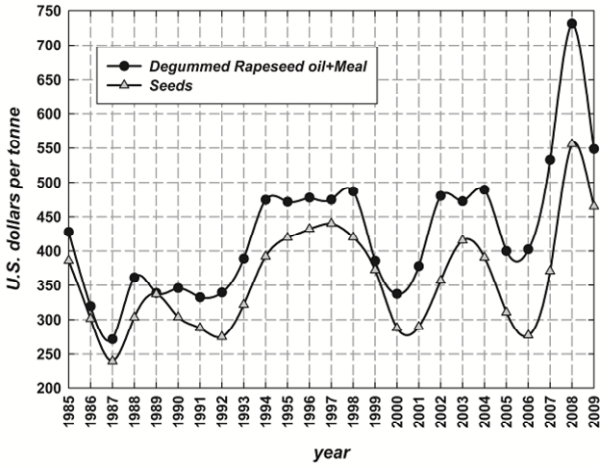

Fig. 4: comparison between input and outputs prices of a refinery producing Rapeseed oil

The Fig. 4 considers 1 tonne of seeds as input, 0.48 tons (oil content in the seeds) of degummed rapeseed oil and 0.52 tons of meal as outputs and it offers some upper limits to estimate the costs and the margins of the process to obtain rapeseed oil.

Table 4 presents a summary of some vegetable oil processing costs. Such data show that the cost to process the vegetable oil represents about the 7-9% of the market price for the rapeseed oil, 6-10% for the sunflower oil and 18-28% for the soybean oil.

Table 4:
processing costs for some vegetable oil variety production with prepress/solvent technology with 24h/day, 300days/year of operation taken from [56]

Rapeseed	tons/day	44	66		
	$/liter	0.16	0.14		
Sunflower	tons/day	500	1000	1500	2000
	$/liter	0.24	0.18	0.16	0.15
Soybean	tons/day	650	1250	1850	2450
	$/liter	0.41	0.33	0.29	0.27

Note: the processing costs are referred to 2008. They have been re-estimated using inflation data [56]

For decades, the technology for obtaining refined vegetable oil remains unchanged, but the final price of vegetable oil undergoes considerable oscillations. For some varieties of vegetable oil the oscillation in the price is linked to oscillation in the price of fossil crude oil. The strength of this dependence depends on the variety of vegetable oil. In fact, the market price of rapeseed oil has a link stronger than the other varieties of vegetable oil with the price of crude oil. Other varieties of vegetable oil are less affected by fluctuations of crude oil because their main use is in food [58]. An increase in the price of vegetable oil also has an impact on biodiesel. However these increases are mitigated by the reduction of the margin for the biodiesel manufacturers. Manufacturers are encouraged to reduce the margin because the price of biodiesel would be intolerable for the customers. Sometimes, to handle short periods of rising prices biodiesel manufacturers uses the credit aging. Thus the biodiesel facilities are stressed by the searching of feedstocks at lower price.

3.3 Special refining processes for biodiesel production

Vegetable oils for biodiesel production must be suitably pre-treated before entering the transesterification process (Fig. 5) [59] whenever feedstock quality and refinement cannot otherwise be adequately guaranteed. This means that the oil sometimes undergoes treatments already implemented in a previous step. The first step is to heat the oil to about 90°C, followed by mixing with a strong mineral acid, which acts as a flocculant clarifying the oil. The acid treatment is used to remove any hydrophobic gums still contained in the vegetable oil. This conditioning step is completed with the mixture stationing in a tank for about 10 minutes.

In the next step the vegetable oil is mixed with NaOH (usually 0.1-0.2% wt) for neutralization. The NaOH enables the removal of free fatty acids that would give problems in subsequent biodiesel

production. Then centrifugation follows to separate the soap of the previous step. Successively water is added and the solution is centrifuged to remove traces of impurities. The washing water is then separated from the vegetable oil by means of a vacuum flash-vaporization process conducted with the oil at 116°C and 0.8-0.9 bar absolute. This makes it possible to reduce the water content to less than 0.1% wt [60]. The oil is often sent to the process plant at temperatures between 40°C and 50°C. It is also best for the oil to be filtered to ensure that no solid particles enter the biodiesel production section [61]. Then, providing its fatty acid content is appropriate (<2.5% wt) [62], the oil can be sent to the transesterification stage.

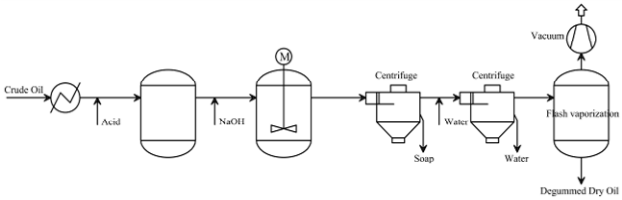

Fig. 5: Vegetable oils neutralization process for biodiesel production.

3.3.1 Esterification

To avoid completely soap formation in the transesterification reactor, the maximum amount of free fatty acids allowable for a system with an alkaline catalyst must be <0.5% wt (acid value<1) [63-65]. If this is not the case, a preliminary esterification treatment is required. In the esterification reaction, alcohols and carboxylic acids convert to give rise to esters [66]. Esterification follows the pattern:

$$RCOOH + R'OH \leftrightarrow R\text{-}COOR' + H_2O$$

The vegetable oil is dried (to water content of 0.4% wt) and filtered before it is loaded into the acid esterification tank, where it is mixed with methanol (molar ratio alcohol to free fatty acids between 20:1 and 40:1) and large quantities of H_2SO_4 (10% wt of the total fatty acids content [67]). The reactor is stirred at about 600 rpm at a temperature of 60°C for 1.5 to 2 hours [68].

The reaction produces water, so the reacting mixture is pumped into a settling tank where the methanol, water and H_2SO_4 separate from esters and fatty acids. The methanol/acid/water mixture being treated can be re-used later to neutralize and acidify the glycerine. The oily phase leaves the settling tank with low free fatty acid content and can be sent to the transesterification reactor. If the free fatty acid content is still too high, a second acid esterification stage is performed. If a two-stage acid treatment is needed, mixing is suspended until after the methanol has been separated and removed. Then fresh methanol and some acid are added once again and the mixing process resumes.

As soon as the reaction has reached equilibrium, the methanol/acid/water mixture is removed by settling or centrifugation.

4. Transesterification

Transesterification is a chemical reaction between an ester and an alcohol that produces a new ester in which reacting alcohol replaces the original alcoholic group. The transesterification process takes place as follows:

RCOOR'+ R"OH ↔ R"COOR + R'OH

Alkyl esters of fatty acids and glycerol are produced when the reaction involves the triacylglycerols in vegetable oils or animal fats. The transesterification reaction of triacylglycerols proceeds as follows:

Triacylglycerol +3 R'OH ↔ Glycerol +3 R'COOR

This reaction actually takes place in three steps, during which unwanted compounds, such as diacylglycerols and monoacylglycerols, also make an appearance [69, 70].

Triacylglycerol + R'OH ↔ Diacylglycerol + R'COOR1
Diacylglycerols + R'OH ↔ Monoacylglycerol + R'COOR2
Monoacylglycerol + R'OH ↔ Glycerol + R'COOR3

The three reactions occur in series for the oil and in parallel for the alcohol. When the oil and alcohol are immiscible, or only partially miscible, the parallel character of the three reactions is evident in the first few minutes, when mass transfer is an important factor in the reaction [71]. To avoid any transport phenomena affecting the reaction times, the reaction is completed under high-speed stirring. After the first few minutes, the serial character of the reaction prevails [72]. As the triglycerides are converted to diglycerides, at the same moment diglycerides are converted to monoglycerides. In the three reactions, the esters increase the miscibility between the compounds of the reaction mixture, acting as solvents for alcohol and glycerides. In this sense the transesterification is a reaction with solvent, in which the solvent is one among the products of the reaction. So the reaction between vegetable oil and reacting alcohol (the rate determining step) is helped by the esters presence and vegetable oil reacts gradually in higher quantities.

Transesterification is an equilibrium reaction so both reagents and products will be present simultaneously when it comes to an end. Since the main products of interest are the esters, the reaction is run with alcohol in excess to increase the proportion of esters at equilibrium [73]. At equilibrium two partially miscible phases are obtained, a glycerol rich phase (bottom) and a esters rich phase (upper). Each phase has a different content of the other compounds present in the reacting mixture [74]. An increase in temperature increases the reaction rate and yield, providing it is consistent with the evaporation temperature of the alcohol adopted. The enthalpy of transesterification reaction is [75] at 40°C -9.8±0.9 kJ/mol for biodiesel formed from rapeseed oil and methanol and -9.3±0.7 kJ/mol when rapeseed oil and ethanol is used. For these kinds of vegetable oil and alcohols the transesterification is a slight exothermic reaction. The reaction is catalyzed by various compounds. The catalyst may be alkaline [76] or acid [77], using biochemical compounds (enzymatic catalysis) [78, 79], or even acid or alkaline compounds that form a heterogeneous solutions with reagents and products [80, 81]. The alkaline catalysts most commonly used in the experimental investigation are: NaOH, KOH, carbonates [82, 83], sodium methoxide and potassium methoxide, while typical acid catalysts include: H_2SO_4, HCl, H_3PO_4 and sulfonic acids [84]. Many of these catalysts are unsuitable for industrial applications [85], which mainly rely on an alkaline catalyst homogeneous with methanol [86]. The reasons why industrial processes use alkaline catalysts are:

- high reaction rate,
- low capital costs [87],
- a high yield,
- a low temperature,
- a low excess alcohol,
- a low corrosive power of intermediate products (which is a major drawback of acid catalysis)
- a quite fast reaction (about 2hours for equilibrium)

In most cases, the alkaline catalyst used is KOH at concentration from 0.1 to 1.5% of vegetable oil mass, and the alcohol involved is in a molar ratio alcohol:vegetable oil of 6:1.

When methanol and KOH are used in a stoichiometric ratio, the transesterification reaction can be rewritten as:

$$\text{Triacylglycerols} + 3CH_3OH \leftrightarrow \text{Glycerol} + 3\ CH_3COOR$$

The product of this reaction is a mixture of fatty acid methyl esters, known as biodiesel; the by-product of the reaction is glycerol, which can be recovered, purified and placed on the market or further processed to produce hydrogen by steam reforming [88, 89] or many other compounds with a

high added value by anaerobic fermentation [90] or by algal metabolism [91]. The kinetic model describing the reactions involved in transesterification follows a second order scheme [92]:

$$\frac{d[TG]}{dt} = -k_1[TG][MeOH] + k_2[FAME][DG]$$

$$\frac{d[DG]}{dt} = k_1[TG][MeOH] - k_2[FAME][DG] - k_3[DG][MeOH] + k_4[FAME][MG]$$

$$\frac{d[MG]}{dt} = k_3[DG][MeOH] - k_4[FAME][MG] - k_5[MG][MeOH] + k_6[FAME][G]$$

$$\frac{d[G]}{dt} = k_5[MG][MeOH] - k_6[FAME][G]$$

$$\frac{d[FAME]}{dt} = k_1[TG][MeOH] - k_2[FAME][DG] + k_3[DG][MeOH] - k_4[FAME][MG] + k_5[MG][MeOH] - k_6[FAME][G]$$

$$\frac{d[MeOH]}{dt} = -k_1[TG][MeOH] + k_2[FAME][DG] - k_3[DG][MeOH] + k_4[FAME][MG] - k_5[MG][MeOH] + k_6[FAME][G]$$

Where TG, DG, MG, MeOH, FAME, G are respectively triacylglycerol, diacylglycerol, monoacylglycerol, methanol and glycerol. Tables 5a, 5b and 6 show some of the most important results for industrial applications obtained from the transesterification of commonly-available vegetable oils with methanol or ethanol and an alkaline catalyst.

Table 5a: Results of alkaline homogeneous alkaline transesterification of sunflower oil with methanol

Reagents		Catalyst	Reaction conditions					Kinetics constants (l/mol*min)						Equilibrium	Ref.
Oil	Acohol		Impeller Speed [rpm]	Alcohol/Oil molar Ratio	Temp. [°C]	Cat. conc. (% wt oil)	Res. time [min]	k1	k2	k3	k4	k5	k6	biodiesel yield (% wt) in res. time	
Suflower Oil	MeOH	KOH [76] [92] [93] [94] [95] Free fatty acid content in oil (% weight) 0.02;saponification value of oil (mg KOH/g) 193.7; iodine value of oil (mg of I2/g) 130.2; peroxide value of oil (mequiv/kg) 17.1; homogeneous mixture with the specified impeller speed	600	6:1	25	0.5	120	0.1	0.3	0.2	0.1	0.2	0.0160		[92]
			600	6:1	35	0.5	120	0.2	1	1.7	2.2	0.3	0.0110		[92]
			600	6:1	45	0.5	120	0.4	1.9	3.8	4.4	0.3	0.0077		[92]
			600	6:1	55	0.5	120	0.8	6	11	16	0.3	0.0035		[92]
			600	6:1	65	0.5	120	1.5	14	23	41	0.4	0.0026		[92]
			600	6:1	25	1	120	0.1	0.4	0.3	0.2	0.3	0.0130		[92]
			600	6:1	35	1	120	0.3	1.5	2.5	3.1	0.4	0.0077		[92]
			600	6:1	45	1	120	0.5	3.1	7	10	0.5	0.0030		[92]
			600	6:1	55	1	120	1.6	8.5	21	23	0.6	0.0012		[92]
			600	6:1	65	1	120	3.1	24	33	58	0.5	0.0009		[92]
			600	6:1	25	1.5	120	0.2	0.7	0.4	0.4	0.5	0.0040		[92]
			600	6:1	35	1.5	120	0.4	2	4.3	4.7	0.6	0.0005		[92]
			600	6:1	45	1.5	120	0.7	5	12	13	0.7	0.0006		[92]
			600	6:1	55	1.5	120	2.1	11	30	30	0.8	0.0001		[92]
			600	6:1	65	1.5	120	4	27	55	66	0.9	0.0001		[92]
			N.R.	7.5:1	65	1.5	60							89.15-89.42	[93] [94]
			N.R.	4.5:1	65	1.5	60							90.7-90.43	[93] [94]
			N.R.	7.5:1	25	0.5	60							99.88-99.28	[93] [94]
			N.R.	4.5:1	25	1.5	60							97.77-97.17	[93] [94]
			N.R.	7.5:1	65	0.5	60							98.32	[93] [94]
			N.R.	7.5:1	25	1.5	60							96.58-96.88	[93] [94]
			N.R.	4.5:1	65	0.5	60							98.7	[93] [94]
			N.R.	4.5:1	25	0.5	60							96.37-96.96	[93] [94]
			N.R.	6:1	45	1	60							98.11	[93] [94]
			N.R.	6:1	78.63	1	60							93.33-94.28	[93] [94]
			N.R.	6:1	11.36	1	60							96.39-97.37	[93] [94]
			N.R.	6:1	45	1.84	60							92.07-92.45	[93] [94]
			N.R.	6:1	45	0.16	60							97.69-97.94	[93] [94]
			N.R.	8.52:1	45	1	60							97.66-97.77	[93] [94]
			N.R.	3.47:1	45	1	60							96.04-83.82	[93] [94]
			600	6:1	65	1	240							91.67±0.27	[76]
			600	6:1	60	1	120							86.7±0.9	[95]
		NaOH [76] [96] [95] [97] [98] [99] [100] Homogeneous mixture with 600 rpm impeller speed	600	6:1	25	0.5	4							86	[97]
			600	6:1	65	0.5	4							98.1	[97]
			600	6:1	25	1.5	4							99.7	[97]
			600	6:1	65	1.5	4							100	[97]
			600	6:1	45	1.71	4							100	[97]
			600	6:1	73.3	1	4							99.7	[97]
			600	6:1	16.7	1	4							96.6	[97]
			600	6:1	45	0.29	11							89	[97]
			600	6:1	30	1	120							90.9±0.8	[95]
			600	6:1	45	1	120							92.8±1.0-97.77	[95] [97]
			600	6:1	60	1	120							97.1±0.9	[95]
			600	3:1	60	1	120							61.5±0.7	[95]
			600	9:1	60	1	120							93.0±1.2	[95]
			600	12:1	60	1	120							86.0±1.5	[95]
			600	15:1	60	1	120							83.8±1.2	[95]
			600	18:1	60	1	120							81.0±0.8	[95]
			600	6:1	60	0.25	120							51.6±1.0	[95]
			600	6:1	60	0.5	120							65.0±0.8-98	[95] [98]
			600	6:1	60	0.75	120							92.9±0.9	[95]
			600	6:1	60	1.25	120							82.7±1.5	[95]
			600	6:1	60	1.5	120							78.1±1.2	[95]

N.R.=Not Reported

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Table 5b:
Results of alkaline homogeneous alkaline transesterification of sunflower oil with ethanol

Reagents		Catalyst	Reaction conditions					Kinetics constants (l/mol*min)						Equilibrium	Ref.
Oil	Acohol		Impeller Speed [rpm]	Alcohol/oil molar Ratio	Temp. [°C]	Cat. conc. (% wt oil)	Res. time [min]	k1	k2	k3	k4	k5	k6	biodiesel yield (% wt) in res. time	
Suflower Oil	EtOH	KOH [98] [101] Free fatty acid in oil (% weight) 0.45; viscosity (40°C-mm*mm/s) 46.61;saponification value of oil (mg of KOH/g) 193.7; Iodine value of oil (mg of I2/g) 89.1; peroxide value of Oil (mequiv/kg) 10.1; homogeneous mixture with 600 rpm impeller speed.	600	5:1	20	0.5	60							76.66	[101]
			600	5:1	32	0.5	60							84.45	[101]
			600	5:1	20	1.5	60							97.53	[101]
			600	5:1	32	1.5	60							95.57	[101]
			600	7:1	20	0.5	60							88.76	[101]
			600	7:1	32	0.5	60							92.65	[101]
			600	7:1	20	1.5	60							89.38	[101]
			600	7:1	32	1.5	60							93.59	[101]
			600	6:1	26	1	60							91.35	[101]
			600	6:1	26	1	60							88.12	[101]
			600	6:1	26	1	60							89.12	[101]
			600	6:1	26	1	60							86.31	[101]
			600	3:1	75	0.5	60							81	[98]
		NaOH [102] Any information about vegetable oil quality	600	6:1	25	0.75		1.742	0.119	$5.74*10^{-3}$					[102]
			600	6:1	25	1		3.254	0.240	$9.03*10^{-3}$					[102]
			600	6:1	25	1.25		4.145	0.371	$11.04*10^{-3}$					[102]
			600	9:1	25	0.75		1.003	0.091	$1.89*10^{-3}$					[102]
			600	9:1	25	1		4.643	0.215	$4.52*10^{-3}$					[102]
			600	9:1	25	1.25		7.736	0.405	$6.06*10^{-3}$					[102]
			600	12:1	25	0.75		3.170	0.140	$11.10*10^{-3}$					[102]
			600	12:1	25	1		6.93	0.327	$45.0*10^{-3}$					[102]
			600	12:1	25	1.25		11.82	0.497	$111.3*10^{-3}$					[102]
			600	6:1	50	0.75		5.18	0.486	$8.16*10^{-3}$					[102]
			600	6:1	50	1		6.04	0.698	$11.1*10^{-3}$					[102]
			600	6:1	50	1.25		6.52	0.938	$12.8*10^{-3}$					[102]
			600	9:1	50	0.75		4.95	0.498	$3.64*10^{-3}$					[102]
			600	9:1	50	1		8.17	0.941	$5.65*10^{-3}$	Kinetics model: pseudo second-order type				[102]
			600	9:1	50	1.25		9.26	1.163	$7.03*10^{-3}$					[102]
			600	12:1	50	0.75		10.8	0.524	$34.5*10^{-3}$					[102]
			600	12:1	50	1		13.5	0.741	$74.4*10^{-3}$					[102]
			600	12:1	50	1.25		17	1.337	$135.4*10^{-3}$					[102]
			600	6:1	75	0.75		6.24	0.891	$12.3*10^{-3}$					[102]
			600	6:1	75	1		7.84	1.165	$14.2*10^{-3}$					[102]
			600	6:1	75	1.25		8.8	1.335	$14.9*10^{-3}$					[102]
			600	9:1	75	0.75		7.5	1.423	$5.72*10^{-3}$					[102]
			600	9:1	75	1		9.57	1.68	$6.43*10^{-3}$					[102]
			600	9:1	75	1.25		12.6	1.921	$7.35*10^{-3}$					[102]
			600	12:1	75	0.75		10.9	1.795	$82.5*10^{-3}$					[102]
			600	12:1	75	1		16.1	2.31	$135.3*10^{-3}$					[102]
			600	12:1	75	1.25		20.8	2.956	$201.4*10^{-3}$					[102]

N.R.=Not Reported

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Table 6:
Results of homogeneous alkaline transesterification of some vegetable oil varieties with methanol and ethanol

Reagents		Catalyst	Reaction conditions					Kinetics constants (1/mol*min)							Equilibrium	Ref.
Oil	Acohol		Impeller speed [rpm]	Alcohol/oil molar ratio	Temp. [°C]	Catalyst conc. (% wt oil)	Res. time [min]	k1	k2	k3	k4	k5	k6	Global rate constant	biodiesel yield (% wt) in specified res. time	
Rapeseed Oil	MeOH	KOH [103] [62]	600	6:1	65	1	120								96	[103]
			600	3:1	65	1	120								57	[103]
		Soxhlet extraction of oil from rapeseed (low erucic acid) with n-Hexane; homogeneous mixture with 600 rpm impeller speed.	600	6:1	35	1	120								90.6	[103]
			600	6:1	50	1	120								93.2	[103]
			180	6:1	65	1	120								81.5	[103]
			360	6:1	65	1	120								96	[103]
			N.R.	6:1	65	1	120								95-96	[62]
	EtOH	KOH [104]	Low	6 (pure):1	30	1	120								91.7	[104]
			High	6 (5% w of water):1	30	1	120								29	[104]
			Low	6 (5% w of water):1	75	1	120								77.8	[104]
			High	6 (pure):1	75	1	120								100	[104]
Soybean Oil	MeOH	KOH [100]	N.R.	6:1	40	0.8	60								95	[100]
		NaOH [105] [106] Free acids in oil 0.09 (% w); The mixture is not homogeneous	300	6:1	50	0.2	90	0.049	0.102	0.218	1.28	0.239	0.007			[105] [106]
Palm Oil	MeOH	KOH [107]	N.R.	6:1	50	1	100	0.018		0.036		0.112	Kinetics model:			[107]
			N.R.	6:1	55	1	100	0.024		0.051		0.158	hydrolisis type			[107]
			N.R.	6:1	60	1	100	0.036		0.07		0.141				[107]
			N.R.	6:1	65	1	100	0.048		0.098		0.191				[107]
		NaOH [108] [109] [100]	350	10:1	60	0.5	25							0.163	98	[108]
			350	10:1	60	0.75	25							0.313	98	[108]
			350	10:1	60	1	25							0.526	98	[108]
			350	6:1	60	0.5	25							0.097	98	[108]
			350	8:1	60	0.5	25							0.147	98	[108]
			350	10:1	70	0.5	25							0.309	99	[108]
			N.R.	6:1	60	1	30								95	[100]
			N.R.	6:1	60	1		0.634	0.000	7.104	4.912	7.860	0.121			[109]
	EtOH	KOH [110]	N.R.	3.6:1	60	1	100								92	[110]

N.R.=Not Reported

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5. Guidelines on the biodiesel production process

It is impossible to describe the processing or purification stages used in biodiesel production because there are many possible solutions that make one facility different from another. However we can compare some reference solutions from which many installations have drawn inspiration referring to the block diagram shown in Fig. 6. About the reaction, the alkaline transesterification of vegetable oil and methanol is the most commonly adopted solution. For the separation units the components involved are mainly centrifugal separators and distillation units. The components and process stages are briefly described in the following paragraphs, according to their specific application in a biodiesel plant.

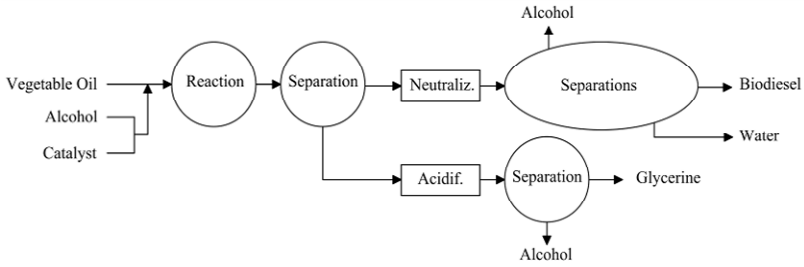

Fig. 6: Block diagram of the biodiesel production process.

5.1 The pumping in biodiesel plants

Centrifugal and volumetric rotary pumps are generally used in plants producing biodiesel: the former are used when no emulsion occurs among the compounds [111]; the latter especially for the transfer of viscous fluids and when a careful flow control is needed to ensure a consistent, low-speed and uniform flow over a wide range of heads, with no pulsing. As usual volumetric pumps are used to deliver the reagents in the reactors. In addition mechanical vacuum pumps or diffusion vacuum pumps are also needed in biodiesel production. Rotary types, mechanical vacuum pumps are present exclusively for the flash distillation units. The type of rotary vacuum pumps most often used are the liquid ring vacuum pumps [112] because in a biodiesel plant the vacuum level is not too low. In fact, in general the minimum vacuum levels generated by liquid ring vacuum pumps (depending on the nature and temperature of the liquid they contain) are higher than 0.08-0.06bar at the vapor pressure of the liquid they contain. Such pressure level is sufficiently below the operational level requested for a biodiesel plant.

5.2 Transesterification reactors

From a chemical and physical viewpoint, knowing the reaction time and how it relates to diffusion mechanisms and transport by convection enables a thoughtful design of the reaction stage [113]. The most important parameters to consider in a reactor are the conversion degree of an interesting reagent and the selectivity of the reaction to the interesting products. The main variables governing the conversion degree and selectivity in the transesterification are temperature, residence time and mixing rate, although for the transesterification the temperature is limited by the evaporation of the alcohol used as reagent and the residence time is limited due to the conversion rate no longer changes significantly after the first few minutes [114]. Indeed the mixing rate is an unconstrained factor which is to maximize. The turbulence by stirring inside the reactor contrasts the immiscibility between the reagents and helps the reaction rate [115, 116]. Obviously also the catalyst influences the yield. Actually the catalysts appeared in the industrial practice are a limited variety of strong homogeneous bases, but in general the transesterification is catalyzed by alkaline- or alkaline-earth-hydroxides like NaOH, KOH, CsOH or RbOH with a little difference in triglyceride's conversion [82]. In the industrial sector just KOH and NaOH are pratically used as catalysts and also the plants born using KOH [117] had used successively NaOH. Nowadays NaOH and KOH are replaced by sodium methoxide (CH_3ONa) due to the absence of water when it is mixed with the alcoholic reagent. The KOH has been dismissed because it produces water when mixed with methanol but especially due to the need to manage the dust in the plant area. So currently the majority of biodiesel plants use CH_3ONa [118].

The two main chemical reactor types, used in the large scale plants, are the stirred batch reactors (BRs) and the continuous stirred tank reactors (CSTRs). Experimentally also the continuous tubular reactors (PFRs), mini and micro-reactors have been successfully tested.

5.2.1 Stirred batch reactors

In a plant with batch reaction the alcohol and catalyst are premixed in a preliminary unit, then the vegetable oil, alcohol and catalyst are sent to the reactor, where they are stirred for about 1h at about 60°C with maximum temperatures around 65°C. Some systems use a two-stages reaction. Nowadays most manufacturers adopt a single stage reaction, with reaction conditions optimized internally to ensure higher yield with shorter reaction times [119]. In some cases, where a two stages reaction is adopted, the glycerine being removed between the two stages, in order to increase the conversion degree of the reaction to around 98-99% and minimizing the reaction-inhibiting effect of the products. In such systems, 80-90% wt of alcohol and catalyst entering the process are added to the oil before loading the first reactor. The reaction products are subsequently taken from the first reactor by

flooding or maintaining a constant level inside the reactor. Before it goes into the second reactor, the outflow of products from the first reactor is sent to the stage for separating the glycerol-rich phase (GL) from the phase rich in esters (BD). The remaining 10-20% wt of alcohol and catalyst are added to the second reactor [120]. Discontinuous reaction systems in current practice use molar ratios of alcohol:vegetable oil ranging from 4:1 to 20:1 [121] with residence times of 30min, although the use of lower molar ratios leads to high enough yields. In fact performing the reaction in two stages with molar ratios respectively 1:4.5 (1% wt KOH respect to the wt of the vegetable oil) and 1:1 (0.2% wt KOH respect to the wt of the vegetable oil) and residence times of 30min, the yield of 98.5% could be obtained [122]. However the trend of the facilities is to decrease the amount of methanol and catalyst for the reaction, increasing the reaction temperature and the stirring. To decrease the methanol amount helps to decrease the energy for the purification of the excess in the distillation column. After the single stage reaction section, the process is continuous thanks to the presence of buffer tanks capable of containing the product coming from 3-4 batch reaction cycles or containing the amount of the products from several alternatively-operated single batch reactions. In fact batch reactors are generally not used for large production rates, for which the separation and purification steps that follow the reaction are much more efficiently operated on a continuous basis. The most used alkaline catalysts are in amounts ranging from 0.1% to 2% wt of alcohol used. At the start of the reaction, thorough mixing is needed to bring oil, alcohol and catalyst into intimate contact. Towards the end of the reaction, a lower stirring speed can increase the conversion degree and facilitate the separation of the GL phase (an inhibitor product of the reaction) from the BD phase [123]. Several studies have been performed on the stirring of the batch reactors because this is one among the most important aspects to maximize the reaction yield. The turbulence induced by a mixer depends on the geometry of the mixer and reaction vessel. Therefore it is difficult to derive just one value of intensity of mixing in terms of rpm able to perform an optimal mixing between methanol and vegetable oil. Some information are reported by [92, 105]. Performing the reaction in simple reactor vessels, mixing the reacting mixture with mechanical stirrers between 300rpm and 600rpm (corresponding respectively to impeller Reynolds numbers 6200 and 12400) the yield increases at higher intensities. For Reynolds numbers higher then 12400 (600rpm), the mixing do not affect the tryglicerides conversion and so the reactor can be considered perfectly mixed. Deeper investigations are in [124] where the flow regime and the drop size are aspects studied in case of the unreacting binary system methanol/vegetable oil and in case of multicomponent and time-dependent reacting mixture. This work states that the behavior of the transesterification can be explained by the increasing of the interfacial area, due to intensive drop breakage process during the stirring. After few minutes the transesterification becomes

slower approaching the state of equilibrium due to the decrease of methanol concentration and the increase of the products.

5.2.2 Continuous stirred tank reactors and other reactors

The CSTRs are used where large production rates are required. The reaction is often conducted using few (2 or 3) CSTRs in a cascade pattern [125, 126]. The first reactor may be of larger volume so that the mixture spends more time in it, thus achieving a higher conversion degree. Then the initial GL phase is separated from the BD phase and carried to a second reactor, where the reaction is fairly rapid and the yield can be as high as 98% [127]. Mixing ensures that the composition inside the reactor is homogeneous, as well as having the effect of increasing the dispersion of glycerine produced in BD, allowing a longer time for the next phase separation. In [128] and experimental activity on a 6-stage continuous reactor (2.272 l) was evaluated. Effects of residence time (3-12 min), stirrer speed (0-800 rpm), and NaOH concentration (0.25-1.0% wt of oil) on yields were investigated at molar ratio of methanol to oil of 6:1 and temperature of 60°C. Higher stirrer speed increased the reaction rate but excessive stirrer speed decreased the reaction rate probably due to the GL phase dispersion. At NaOH of 1.0 wt% of oil, the reactor could produce biodiesel at purities ranging from 97.5% to 99.2 wt% within residence times of 6-12 min. Other continuous reactors which improve the surface contact between reagents have been tested with good results. Atomizing the oil and in contact with methanol vapours at 70°C-90°C it is possible obtain the 96% of triglycerides conversion with a residence time of few seconds [129].

The PFRs is another type of continuous reactor where the mass flow through each area of the reactor is always the same [130, 131]. Industrial applications of the PFRs reactor have been proposed [132] but effective installation are not existing. Various kind of tubular reactors was experimented. With fixed-bed plug flow reactors [133] a yield of 91.7% can be obtained within 19min of residence time, 65°C, 1.2%wt of KOH and molar ratio methanol:rapeseed oil 6:1.

Using the micromixing effects gives high reaction yields. In [134] corrugated plates heat exchanger as a reactor was adopted. Reynolds numbers between 9 and 17 was realized in a very compact tubular reactor.

5.3 Separation of the BD phase from the GL phase

The products emerging from a transesterification reactor can easily form an emulsion, especially if they come into contact with water [111]. These problems are reduced by using volumetric gear pumps. The presence of significant quantities of mono-, di- and triacylglycerols in the final mixture can lead to a layer of emulsion forming at the interface between the BD and GL phase. This layer is

bound to mean a loss of product if it is not recovered and separated. In the worst cases, the resulting biodiesel fails to comply with the specific legislation and has to be processed again. If this problem crops up, the whole reaction needs to be redesigned to improve the triacylglycerols conversion degree. After the reaction, the GL phase is removed from the BD phase. The closer the pH of the reaction mixture to neutral, the faster the coalescence of the GL phase will be: this is one of the reasons for reducing the total quantity of catalyst in the reaction. Given the low solubility of glycerol in esters, separation does not usually take long and it can be done directly in the reactor, or in a settling tank at small plants, or through a centrifuge in case of continuous installations. The presence of methanol in both phases increases the solubility of ester and glycerol [135]. The BD phase is quickly separated from the GL phase, effectively exploiting the difference in density between the two phases (about 880 kg/m^3 for the BD phase and 1050 kg/m^3 for the GL phase). The centrifuge completes this operation on a mixture with a temperature of 50°C-60°C and can also separate the solids that accumulate on the outer edge of the centrifuge drum. The excess methanol tends to act as a solvent, slowing down the separation process, but the excess methanol is typically not removed from the product flow before the GL and BD are separated to avoid reversing of the transesterification reaction. After it has been separated from the GL, the BD goes to a neutralization stage, where H_3PO_4 is used because the resulting K_3PO_4 can be used as a fertilizer. In case of NaOH or CH_3ONa catalysts there is not formation of fertilizer and the salts are considered waste, so in these cases, the neutralization is performed with citric acid powder. However in some discontinuous systems, the reaction mixture is neutralized before the BD and GL phases are separated.

Immiscible or only partially miscible compounds with different densities in solid and liquid phase are separated by means of centrifugal units. The compounds fed into the separators are submitted to a centrifugal forces field at a speed represented by the Stokes law [136]. In the case of a liquid-liquid system, the mechanism is no different from that of a solid-liquid system, except for the fact that droplets of liquid are moving instead of solid particles. These droplets move throughout a liquid phase and give rise to another phase by coalescence.

The disk centrifuge handles larger flow rates and turns at lower speeds, developing centrifugal forces up to 7000 times the force of gravity. It can manage up to $20m^3h^{-1}$ of input containing moderate amounts of solid matter, which is downloaded continuously in the form of mud. Such centrifuges are designed mainly for liquid-liquid systems, but they can also be used in liquid-liquid-solid or liquid-solid systems if the end product to obtain is a clarified liquid. Disk centrifuge is the type most often used in biodiesel production plants [137].

5.4 Recovering excess alcohol from biodiesel

After separating the GL and neutralization, the BD enters the methanol separation stage, which is usually a stripping process or vacuum flash vaporization, in the classic version or in a falling film evaporator. The molar fraction of methanol in equilibrium with the biodiesel is very low for lower than atmospheric pressures. The alcohol recovery process may be preceded by a process of acidification to remove any soap in the biodiesel. The free fatty acids remaining in the BD phase and the salts will be removed afterwards by washing with neutral water. If the amount of soap is limited, this stage may not be necessary, but if it is considerable (>1000ppm), then the soap would risk causing "foaming" inside the flash separation tank. Removing the methanol in the flash separation tank might also make the soap remaining in the BD phase solution precipitate, clogging the filters and sieves.

5.5 Ester washing

The water used in the ester washing process is at 50-60°C and has a slightly acidified pH (3-6% wt of H_2SO_4 or HCl) to remove any soap that might form during the reaction and to neutralize any contaminants. e.g. calcium and magnesium, the catalyst, the salts and free fatty acids. The salts will be removed by the water, and the free fatty acids will remain in the BD. This rinsing with water also enables any residual methanol and free glycerine to be extracted from the BD, although this methanol will need to be removed from the water before the washing stage to prevent it from getting into the wastewater. The neutralizing process adopted before the washing cycle reduces the washing water consumption and minimizes any formation of emulsions in subsequent purification stages. The BD phase then undergoes water separation, which is often done by a centrifuge operating at a temperature of >40°C and capable of separating any solids accumulating on the outer edge of the drum as well. Then the BD, consisting by now almost entirely of esters, can come into contact with clean water again (which must still be separated). Later in the washing process, any remaining water (usually <3500ppm) is eliminated from the BD by drying [138], thus obtaining biodiesel. The methanol is recovered from the washing water using a distillation column.

5.6 Ester drying

The simplest approach to drying BD is to use an isotherm flash evaporation unit. Vacuum evaporators are commonly used for high-capacity operations. These systems operate at lower pressures to allow for the water to evaporate at temperatures below 100°C. An alternative to heating and evaporation is to use a thin-film evaporator under vacuum conditions. When the BD (now mainly consisting of ester) is poured into the evaporator, its direct contact with the walls makes its ~~heated~~ water content

evaporate rapidly. Since the total amount of water remaining in the biodiesel after the separation is low, adsorbent materials can also be used to remove these traces of water.

5.7 Adding oxidation inhibitors

Biodiesel contains a large number of molecules with double bonds, so it is susceptible to oxidation [139]. This effect is increased particularly when the esters are exposed to light and air [140] or still contain traces of free fatty acids [141]. Fig. 7 shows the typical oxidation behaviour of vegetable oils and animal fats [142]. Biodiesel follows the same degrading path. The oxidation process is monitored by measuring the peroxide level, or the fraction of oil or biodiesel converted into peroxide molecules (H_2O_2), the first step in the oxidation process. Vegetable oils, animal fats and biodiesels have a so-called induction period, in which no conversion occurs, after which oxidation rapidly sets in. Once peroxide appear, then they decompose in aldehydes. Some of the oxidation inhibitors typically used with lipids in the food industry are butylated hydroxyanisole (BHA), butyl hydroxytoluene (BHT), propylgallate (PG), the tertiary butyl hydroquinone (TBHQ), pyrogallol (PY) [143], Tinuvin P and benzotriazol [144]. It is possible also to adopt natural oxidation inhibitors like the tocopherols [145], but they deteriorate quickly increasing temperature and pressure. The most effective additive for use in foodstuffs is TBHQ [146]. The same additives have been used for biodiesel antioxidation too [147-149]. However effectiveness of the antioxidants is TBHQ>PY>PG [150].

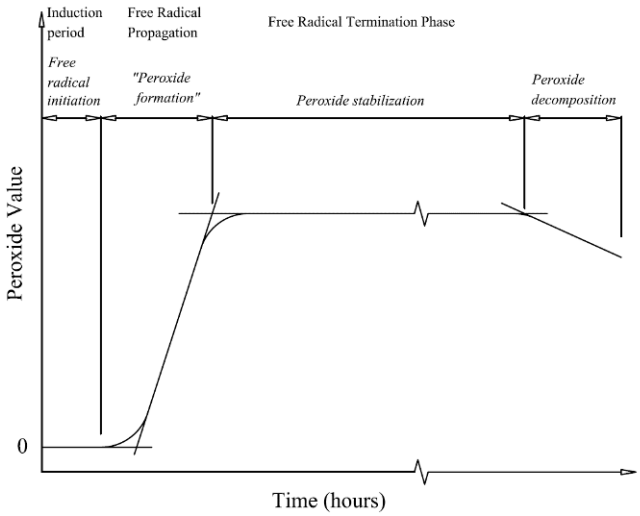

Fig. 7: Effect of time on peroxide formation and decomposition.

5.8 GL phase acidification

At the end of the reaction, the alcohol content in GL phase is much higher than in BD phase. The GL phase leaving the separator is only 50%-60% glycerol and contains some of the excess methanol and most of the catalyst and soap [151]. These features make its value limited and its disposal difficult. The first GL phase refining stage usually involves adding acid to convert the soap into free fatty acids and salts. These free fatty acids are insoluble in GL phase, so they can be separated, removed and recycled. The fraction rich in free fatty acids collects on the surface of the GL phase and can be removed and recycled in the esterification process [152]. These free fatty acids should be less than 1% of the obtained biodiesel.

5.9 Separation of the alcohol from the GL phase

After acidification and free fatty acids separation, the methanol can be removed from the GL phase. It is better to do this after acidification, because removing the methanol while the GL phase still contains soap leads to the solidifying. First, the liquid mixture is heated up to 90°C-120°C, then the heated liquid is sent through a pressure-reducing valve into a tank. The drop in pressure induced by the valve makes the more volatile part of the liquid evaporate. This takes place in a vacuum. At this point, the GL phase would consist of glycerine with a purity nearing 85%, which can be sold as crude glycerine. The glycerine refining process can be taken further, aiming for a purity of more than 95.5%-97.7%, by means of a vacuum distillation or an ion-exchange process, but it is only worth reaching such levels of purity if the glycerine is to be used by the pharmaceutical industry. If such an option is of interest, this would demand purifying the glycerine to at least 99.5%, as required by the European Pharmacopoeia. The methanol removed from the flows of BD phase and GL phase tends to collect all the water that may have entered the process. This water has to be removed in a continuous distillation column before the methanol is recycled in the process. The methanol recovered must have a water content <0.1% wt, so that the water in the reagent mixture is minimal during transesterification [153, 154]. This phase is much more complex if ethanol has been used as the alcohol, because it forms an azeotrope with water. In such case a pressure swing adsorption system is used to remove the water [155, 156].

5.10 Alcohol purification

In case of methanol continuous distillation is the separation technique used for the purification before the reaction. This is the component with higher thermal power requirement [157] and also the bulkier. In fact to separate methanol and water sufficiently need from 15 to 30 trays, a reflux ratio ranging between 0.8 and 5, temperature from 110°C to 130°C depending on the pressure in the column

(commonly atmospheric). Such conditions are needed to decrease the chemical oxigen demand (COD) load in the wastewater and so to decrease also the remediation treatments of the wastewater. Tipically the residual methanol content in water is below the 5% wt. This flow rate of wastewater can be mixed with the glycerine final stream to adjust the purity at some levels. To adopt this solution allow an high saving on disposal costs. Kettle reboilers are most often used in the distillation columns in the biodiesel industry. Boiling occurs on the shell side, thus enabling any suspended matter to be deposited on the bottom without influencing the heat exchange. The liquid to be vaporized flows just once through the heat exchanger, making kettle reboilers suitable for thermo-unstable fluids such as those derived from vegetable oils [158, 159].

6. Three basic plant process flow diagrams

The ASPENPLUS software was used to simulate the three most widely adopted continuous biodiesel production processes, conducting a sensitivity analysis on these three processes to quantify the response of their various units in different operating conditions. This analysis is useful in enabling a more efficient planning of the production process. ASPENPLUS enables us to define in detail all the necessary components, the thermodynamic models behind the operation of the system components chosen, and all the chemical and physical properties of the compounds involved in the process. Plant design starts with a description of its process flow diagram, i.e. the position and type of the units needed for the production process. Then the behavior of some of these units can be analyzed to see how certain parameters involved in the process respond to change. The compounds chosen from the ASPENPLUS database were methanol, KOH, glycerol, biodiesel, K_3PO_4, H_3PO_4 and vegetable oil. Special attention was paid to define the vegetable oil and the biodiesel. We chose to define the vegetable oil as a set of compounds derived from oleic acid because thermodynamically-reliable experimental data are available, while this is not the case of varieties of compounds derived from other fatty acids. Triolein has also been partially defined in the ASPENPLUS database. The same approach was applied to the biodiesel as for the vegetable oil. We considered a mixture of esters derived from different fatty acids coming from a vegetable oil: assuming that triolein was the only compound in vegetable oil, the biodiesel would consist of methyloleate alone. The proper functioning of each component relies on the choice of thermodynamic model used to describe the chemical and physical conversion of the mixtures. The choice of thermodynamic model depends on the nature of the compounds and the thermodynamic system's working conditions. In the literature there are few experimental data on the phase balance involved in the systems considered [160, 161]. The A-UNIFAC (UNIFAC with the Association activity coefficient model) and GCA-EOS (Group Contribution Association Equation Of State) models have a good predictive capacity for the

compounds and the thermodynamic conditions considered [162], but the A-UNIFAC model is not available in ASPENPLUS. The most suitable model in ASPENPLUS is the UNIFAC-Dortmund [163], the use of which can overcome the limits of the original UNIFAC-VLE [164] and UNIFAC-LLE [165] and predict the phase equilibria of heterogeneous multi-component systems at the working temperatures involved in the installations and for the compounds considered here.

6.1 Set-up of common components

The plants analyzed refer to a mass flow rate of the vegetable oil of 2 tons h^{-1} and assuming a continuous operation. We chose to have transesterification take place in two heated reactors. The refined vegetable oil is sent at 20°C by a positive-displacement pump to the first reactor. The MeOH is conducted with a centrifugal pump inside 2 mixers, adding 30kg of KOH (in solid flakes) or catalyst in a proportion of 1.5% wt of the oil to each mixer through a hopper. The solution required for the first reaction is delivered by a positive-displacement pump to the first reactor, already mixed in a static mixer with vegetable oil in molar ratio of 6:1. The reactor is stirred at 1000 rpm. Before entering the reactor, the mixture passes through a heat exchanger that warms it to 60°C. The triolein conversion degree in the first reactor (REAC-01) is about 86% and the residence time approximately 30 minutes. The products of the reaction are transferred by a positive-displacement pump to a first centrifugal separator (SEP-01), where the BD and GL phases are separated. En route, the BD is mixed in a static mixer with a new alcohol-catalyst solution (adding another 30 kg of KOH to the MeOH delivered by a positive displacement pump that mix the vegetable oil and methanol in a molar ratio of 20:1. The reaction mixture passes through a heat exchanger that warms the fluid up to 60°C. In this second reactor, a triglyceride conversion degree of 96% is reached with a residence time of 30 minutes [166]. After this stage, there is another centrifugal unit for separating the GL phase from the BD phase. This separation can also be done by gravity, which would reduce the energy consumption of the process, but increase its operating times. Considering the dependence of the first separation (SEP-01), performed at 1bar, on temperature (Fig. 8), it is evident that a lower temperature does not significantly affect the amount of glycerol obtained, but it does affect the methanol content in the GL phase.

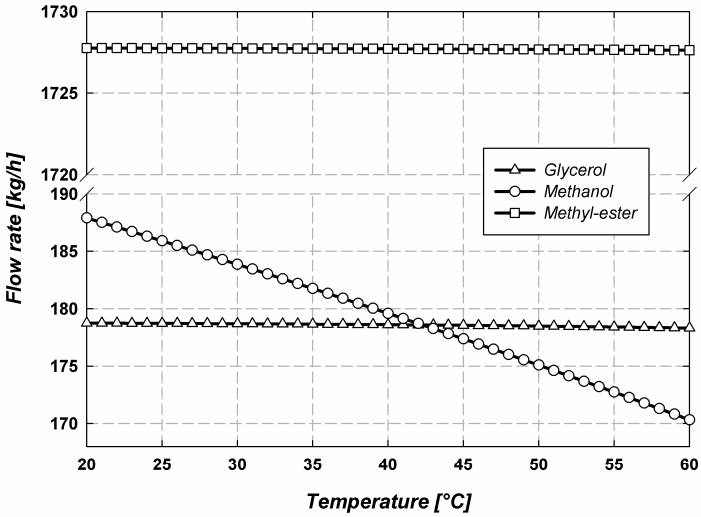

Fig. 8: Temperature dependence of separation SEP-01.

In the second separator, which also operates at 1bar (SEP-02), as shown in Fig. 9, the separation temperature affects the ester content in the BD phase and this affects all subsequent purification stages.

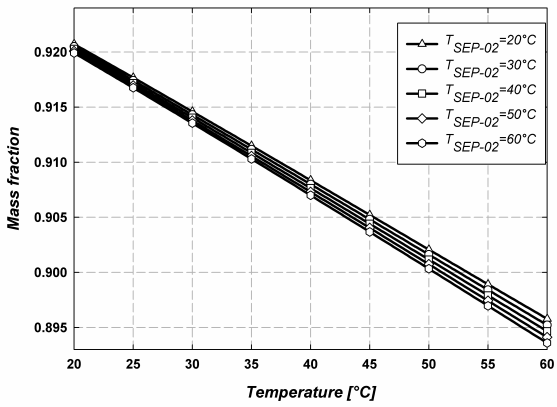

Fig. 9: Effect of temperature change on ester mass fraction separation out from SEP-02.

6.2 Process flow diagram 1

Once separated, the BD and GL phases undergo a series of different treatments (Fig. 10). The main stream produces biodiesel from the BD phase. The BD phase is rinsed with water (L1-WASH) to

remove all residual methanol, catalyst, glycerol and soaps. So first additives are added to the obtained biodiesel, and then it is dried at 120°C and 200mbar (L1-DRYER) to remove all traces of the washing water, and it is finally filtered. The secondary stream from the process involves treating the GL phase adding 50% wt of an aqueous solution of H_2SO_4. This acidification process is carried out in a tank, stirring the mixture, at a temperature close to the reaction temperature and at atmospheric pressure (L1-NEUTRAL). Three different phases can be obtained: a lower GL phase, an upper free fatty acids phase, and a solid precipitated salt phase (K_3PO_4). The mixture undergoes centrifugation to separate the solid precipitate. The GL phase is then sent for flash distillation (L1-FLASH-02) to recover the methanol. If the vegetable oil has a high content of free fatty acids, the GL phase is heated to 110°C and 0.4bar after this distillation process, thereby achieving two distinct phases, one of fatty acids and the other of glycerine (with a purity of about 85%) for further separation. The methanol-rich flow in the vapour phase leaving the flash distiller is mixed with washing water from the stream involved in the BD phase, which has been neutralized with H_2SO_4 to eliminate any traces of catalyst and convert the traces of soap into free fatty acids. Then, the whole water and methanol mixture is treated in a distillation column to recover methanol with a purity >99.99%.

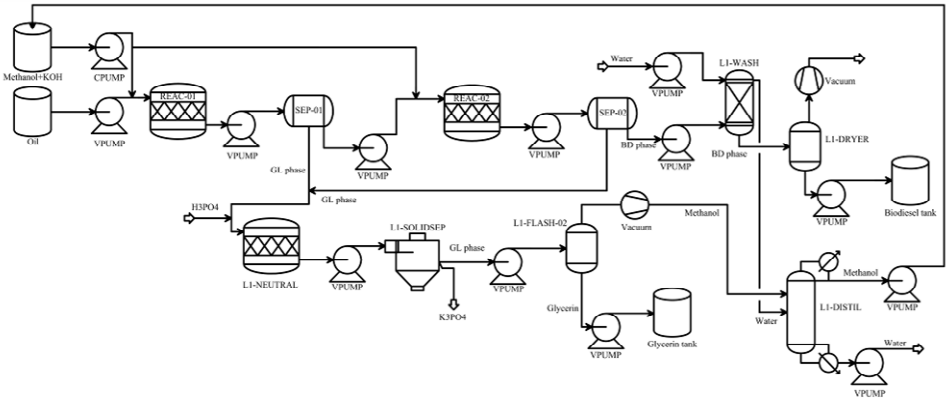

Fig. 10: Process flow diagram 1.

6.2.1 Washing column L1-WASH analysis

The washing column extracts the methanol and any impurities from the BD phase. As seen in Fig. 11 and Fig. 12, increasing the temperature of the process negatively affects the washing conditions, so this should be done using water and BD phase at low temperatures to achieve the maximum content of methyl-esters and the minimum content of water and methanol in the BD phase.

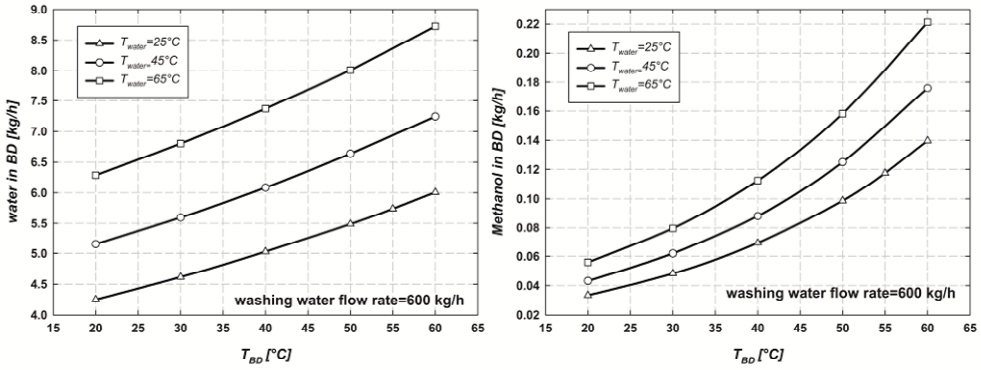

Fig. 11: Mass flow rate of water (left) and mass flow rate of methanol (right) in BD phase after washing with 600 kg/h of water for various inlet temperature of BD phase and washing water.

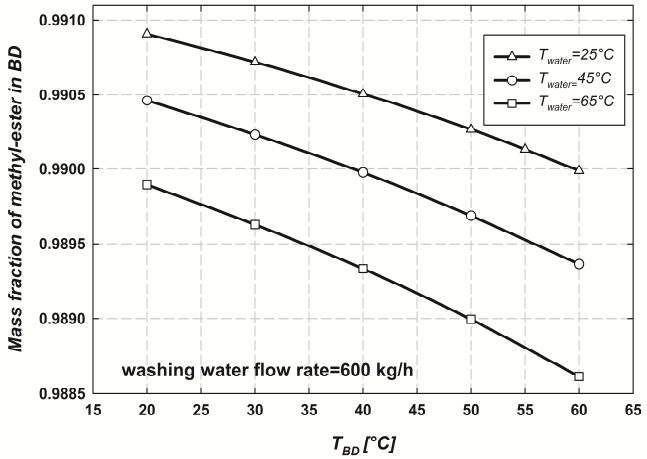

Fig. 12: Mass fraction of methyl-ester in BD phase with 600 kg/h of washing water for various inlet temperature of BD and washing water.

Considering a temperature at 25°C, Fig. 13 shows that increasing the washing water flow gives a better product, rich in esters and almost all the methanol can be extracted. The results confirm the validity of the current practice of using water in quantities equating to one third by mass of the phase being washed.

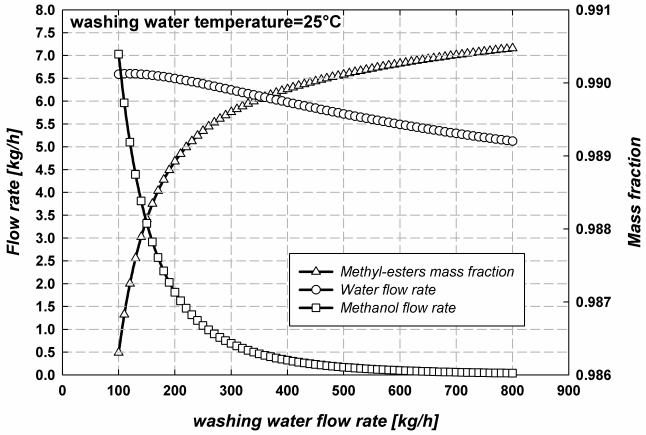

Fig. 13: Mass fraction of methyl-ester, mass flow rate of methanol and water in BD phase for various mass flow rate of washing water.

6.2.2 Dryer L1-DRYER analysis

The flash evaporator named L1-DRYER in process flow diagram 1 separates water from the ester to comply with the standards, i.e. a specific content <500mg/l. For a given washing water flow rate, Fig. 14 and Fig. 15 show the variations of the water content in the BD phase after the dryer, evaporating at 150°C and various pressures, and considering the BD phase at 40°C and 60°C, respectively.

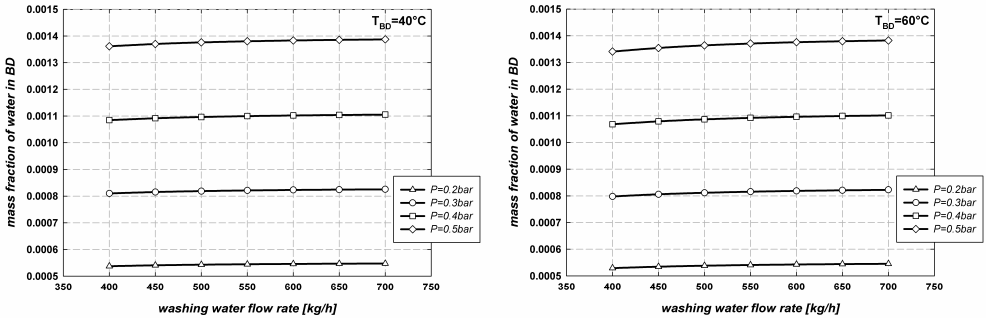

Fig. 14: Water mass fraction in BD phase in relation to water flow rate and drying pressure with BD phase at 40°C (left) and 60°C (right).

As shown in Fig. 15, completing this operation at 115°C and 0.1bar avoids the risk of methyl-ester deterioration due to temperatures above 150°C-250°C being reached [167]. By washing the previous stage with 600 kg/h of water at 25°C and evaporating under a vacuum with an input temperature of

the BD phase set at 60°C, the water content in the BD leaving the evaporator can be controlled by adjusting the pressure and drying temperature.

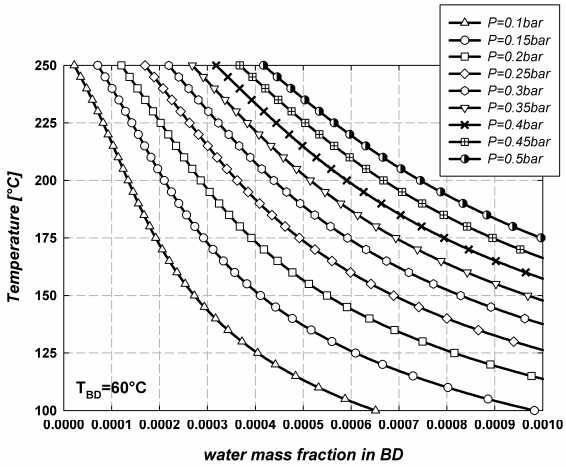

Fig. 15: Water mass fraction in BD phase at various temperatures and pressures.

6.2.3 GL phase flash evaporator L1-FLASH-02 analysis

The flash evaporator for separating the glycerine from the methanol must be able to obtain a glycerine containing glycerol in quantities higher than 85% wt, which is suitable for industrial purposes. Fig. 16 shows how temperature and pressure affect the glycerol content in the GL phase.

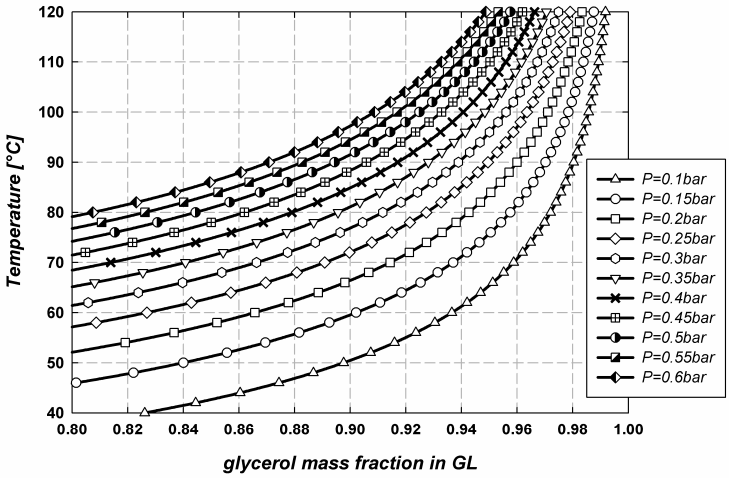

Fig. 16: Glycerol mass fraction in GL phase at various distillation temperatures and pressures.

Design decisions usually go for a pressure of 0.5bar. Fig. 17 shows that the mass fraction of glycerol is more sensitive to pressure changes at low pressures. At 0.1 bar, a 0.05bar variation produces a 2%

change in the mass fraction of glycerol, while at 0.5bar the same pressure change produces a 0.4% change in said fraction of glycerol.

Additional operations, such as filtration and/or bleaching, are needed to obtain a glycerine with a purity higher than 85% (i.e. to reach the >99.5% grade required in the pharmaceutical field).

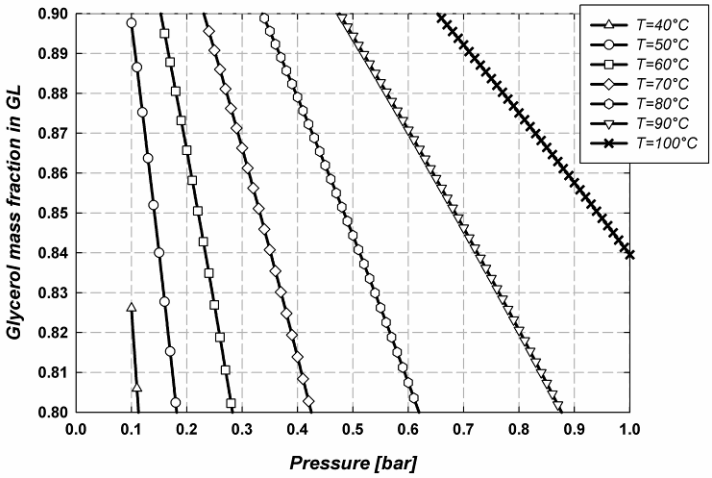

Fig. 17: Glycerol mass fraction in GL phase at various pressure changes.

6.3 Process flow diagram 2

Process flow diagram 2 (Fig. 18) was studied assuming the same initial conditions as in the previous case, and the part concerning the transesterification reaction and the GL phase refining line remained the same. The BD phase leaving the second separator is sent, in this case, to a flash evaporator (L2-FLASH-01), where methanol is separated from the BD before the latter is rinsed with water (L2-WASH) to remove any remaining impurities. The resulting biodiesel is then dried (L2-DRYER).

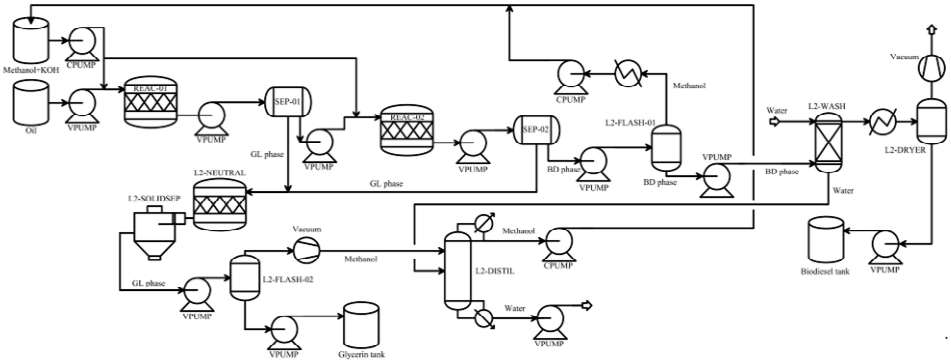

Fig. 18. Process flow diagram 2.

6.3.1 Flash evaporator L2-FLASH-01 analysis

The methanol in the BD phase is recovered by flash evaporation after the separator SEP-02. Fig. 19 shows that changes in the pressure and temperature conditions influence the purity of the methanol sent to the reactor.

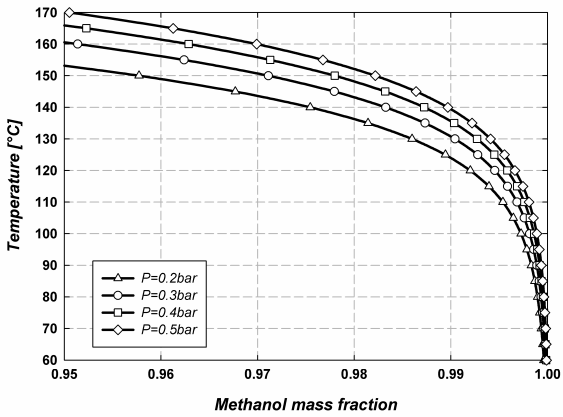

Fig. 19. Methanol mass fraction in vapour phase from L2-FLASH-01 at various temperatures and pressures

6.3.2 Washing column L2-WASH analysis

Any methanol and glycerol still contained in the BD phase is extracted in the washing column. As shown in Fig. 20, using more water ensures a lower methanol content in the BD phase. In addition, a lower temperature of the BD phase at the inlet of the washing column allows less water to be used.

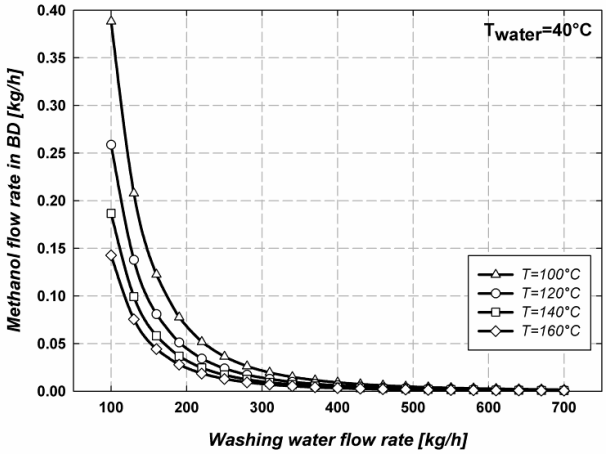

Fig. 20. Methanol mass flow rate in BD phase from extraction column in relation to the water flow rate and the inlet temperature of BD phase considering a water temperature of 40°C

6.4 Process flow diagram 3

In process flow diagram 3 (Fig. 21), after the second separator (SEP-02), the reaction products are sent by a positive-displacement pump to a neutralizing reactor, where a strong mineral acid (H_3PO_4) is added (0.2-0.3% wt) to remove soaps and create an acidic pH to inhibit foam formation. The subsequent vaporization (L3-FLASH-01) is implemented in a range of temperatures between 80°C and 90°C and enables all the methyl alcohol in excess to be removed. The unit operates in a vacuum at 0.1bar. The condensed methanol is collected in a tank at a temperature of 25°C. After adding a dose of water around 10% wt, the BD phase is sent by the positive-displacement pump to a centrifugal separator or washing column (L3-WASH). These treatments clean the BD phase from the glycerol in solution. Since some water remains in the BD phase (mainly esters) the product needs to be dried. A positive-displacement pump is used to pump the mixture of esters and water now comprising the BD phase to a dryer at 115°C, heating the mixture to 95°C through a heat exchanger en route. The dryer operates in a vacuum at 0.01bar, obtained with a liquid ring pump. The GL phase, on the other hand, is sent to a flash evaporator (L3-FLASH-02) at 90°C to separate the methanol and, after condensing, it returns to the service tank. The biodiesel obtained using this system has a purity >99% and a free glycerol content <30ppm.

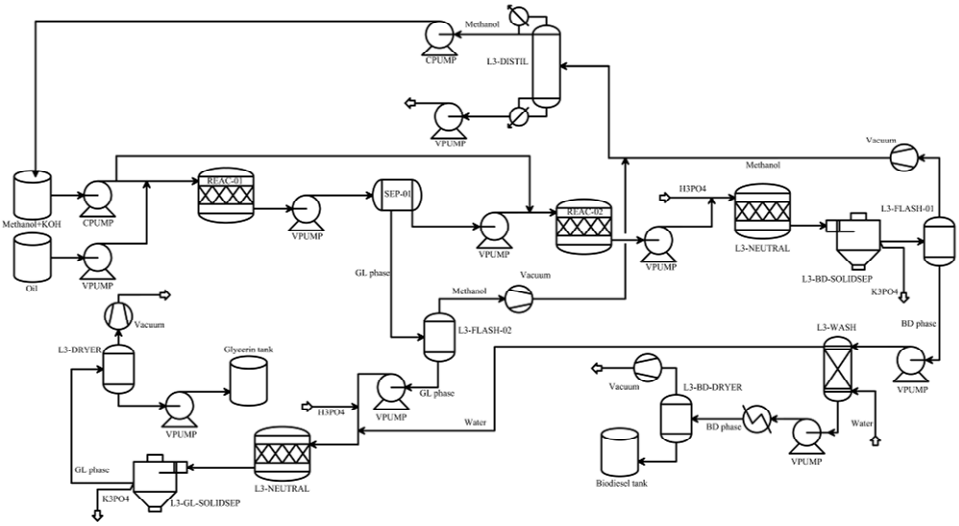

Fig. 21. Process flow diagram 3.

6.4.1 GL phase flash evaporator L3-FLASH-02 analysis

This separator is for evaporating the methanol from the glycerine by flash evaporation to obtain 99.9% of pure methanol in the vapour phase and glycerine with a purity of 80-88% in the liquid phase. Fig. 22 shows how increasing the working temperature improves the purity of the glycerine.

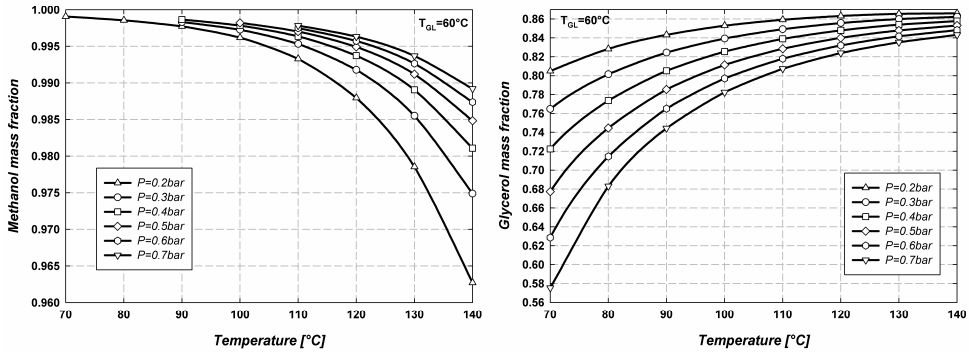

Fig. 22. Methanol mass fraction (left) and glycerol (right) in the liquid phase at various temperatures and pressures with GL phase at 60°C.

6.4.2 Glycerine drying L3-DRYER analysis

Using an acidification unit enables K_3PO_4 to be obtained from the catalyst in the GL phase [168, 169]. This stage involves adding water to dilute the H_2PO_4. It is consequently necessary to include another flash evaporator for the drying of the glycerine. Fig. 23 shows that this process can be run under conditions of moderate vacuum and temperature.

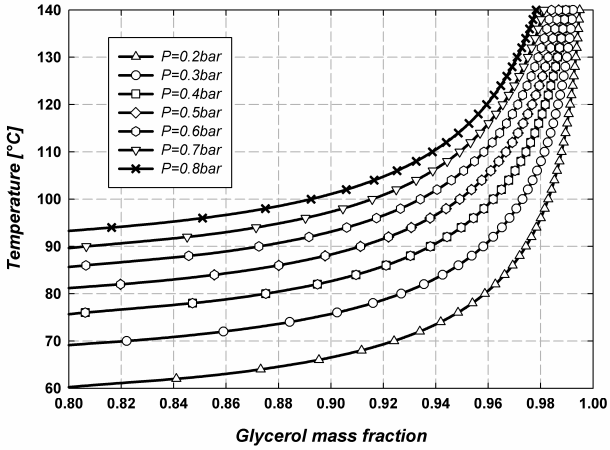

Fig. 23. Glycerol mass fraction in GL phase at various drying temperatures and pressures.

7. Standardization of biodiesel

The standards EN 14214:2008 e ASTM 6751 07b show clearly the correct composition of biodiesel. The biodiesel facilities are stressed customers on the production of biodiesel with quality levels higher then the quality suggested by the standards. Some details about the quality levels for a marketable biodiesel, are reported in table 7. Here the standards levels are compared with the market limits.

Table 7:
Quality of biodiesel reported in the standards and required by market

		EN 14214:2008	ASTM 6751 07b	Market limits	
Density (15°C)	g/cm^3	0.86-0.90			
Viscosity (40°C)	mm^2/s	3.5-5	1.9-6		
Distillation	% (°C)		90% (360°C)		
Flash point	°C	>101min	>93min	>120min or >130min for marine	
Sulphur	mg/kg	≤ 10	≤ 15	≤ 5	Required by few customers for high quality product
CCR 100%	% m/m		≤ 0.05		
Carbon residue (10%dist.residue)	% m/m	≤ 0.3		≤ 0.15	Required by rare customers for high quality product
Sulphated ash	% m/m	≤ 0.02	≤ 0.02		
Water	mg/kg	≤ 500	≤ 500	≤ 300	
Total contamination	mg/kg	≤ 24		≤ 10	Required rarely
Cu corrosion max	3h (50°C)	1	3		
Oxidation stability	h (110°C)	≥ 6	≥ 3	≥ 10	Required by few customers for high quality product
Cetane number		51 min	47 min		
Acid value	mg KOH/g	≤ 0.5	≤ 0.5	≤ 0.30	
Methanol	% m/m	≤ 0.2	≤ 0.2		
Ester content	% m/m	≥ 96.5			
Monoglyceride	% m/m	≤ 0.8		≤ 0.40	
Diglyceride	% m/m	≤ 0.2			
Triglyceride	% m/m	≤ 0.2			
Free glycerol	% m/m	≤ 0.02	≤ 0.02		
Total glycerol	% m/m	≤ 0.25	≤ 0.24		
Iodine value	g I_2/100 g	≤ 120		≤ 115	Required by rare customers for high quality product
Linoleic acid methyl ester	% m/m	≤ 12			
C(x:4) & greater unsaturated esters	% m/m	≤ 1			
Phosphorus	mg/kg	≤ 4		≤ 10	
Gp I metals (Na, K)	mg/kg	≤ 5	≤ 5	≤ 2	
Gp II metals (Ca, Mg)	mg/kg	≤ 5	≤ 5	≤ 2	

8. Conclusions

Alternative fuels are gaining in importance due to unstable crude oil prices and the consequences of emissions deriving from crude oil compounds. Many studies have shown that triacylglycerols are promising sources for the production of alternative fuels. One possibility involves the transesterification of vegetable oils with alcohol catalyzed by basic homogeneous compounds to obtain esters of fatty acid. This method of catalysis is preferable to others because of its high yield and relatively low installation costs [170]. Designing large-scale biodiesel production plants of this type requires a preliminary design effort based on data that are currently incomplete in the technical and scientific literature. This difficulty is compounded by the need to know the chemical and physical characteristics, composition and purity of the vegetable oil used, which also depends on how the oil is extracted and refined. The above-mentioned issues affect how the raw material is converted and purified to produce biodiesel, which can be done in various ways. Sometimes these plants are not optimized, however, giving rise to an end-product that only complies with the specifications dictated by the standards EN 14214:2008 and ASTM D 6751 07b if a great deal of energy goes into the process, and that carries the risk of creating conditions leading to the product's deterioration. An analysis of the main elements involved in such systems emphasizes how they react to changes in operating conditions to obtain a product with the necessary characteristics. Starting from the results discussed, the operation of a given plant can be optimized to achieve the best possible purity of the end-product with the minimal energy expenditure [171, 172].

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